UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CENTER FOR ENVIRONMENTAL MEASUREMENT AND MODELING
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
RESEARCH AND DEVELOPMENT

May 12, 2020

Ms. Cristina Fernandez, Director
Air Protection Division
U.S. Environmental Protection Agency Region 3
1650 Arch Street
Mail Code: 3AP00
Philadelphia, PA 19103-2029

Subject: WV DAQ Data Report #1: Targeted Analysis of PFAS in EPA Method 0010 Sampling Trains Collected at the Chemours Washington Works Facility

Dear Director Fernandez:

I am pleased to provide the enclosed first report from our ongoing collaborative technical support to the West Virginia Department of Air Quality (WV DAQ) assisting with concerns about environmental contamination associated with per- and polyfluoroalkyl substances (PFAS) that may have occurred via air emissions from the Chemours Washington Works facility near Parkersburg, West Virginia.

This report is in response to an August 2018 request from WV DAQ asking for laboratory assistance analyzing PFAS in samples collected during air emission testing at the Chemours facility. The enclosed Report #1 provides targeted analysis laboratory results that quantify various PFAS found in air emission samples collected by Chemours contractors using EPA Method 0010 (also referred to as Modified Method 5 or MM5) sampling train protocols and provided as split samples by TestAmerica to the US EPA.

It is our understanding that this information was requested by WV DAQ to help in their ongoing investigation into the presence of PFAS in the environment near the manufacturing facility of interest. This request relates to our research capabilities and interests applying targeted and non-targeted analysis methods for discovery of the nature and extent of PFAS environmental occurrence that may be potentially associated with industrial releases. EPA continues to develop analytical methods for many PFAS compounds in various media including some of those included in this report. We are providing the results of our analysis as they become available.

In this report, we provide PFAS identification and quantitative analytical results for 2 PFAS (PFOA and HFPO-DA) in 116 MM5 samples. We do not interpret exposure or risk from these values. EPA does not currently have final health-based standards, toxicity factors, or associated risk levels for PFAS, other than perfluorooctanoic acid (PFOA), perfluorooctane sulfonate

(PFOS), and perfluorobutanesulfonic acid (PFBS). While the data provided in the attached report indicates the presence (or lack) of PFAS in the samples, we do not have sufficient information to offer interpretations related to human or environmental exposure and risk.

Thank you for inviting us to be part of this effort that helps to further both EPA's and West Virginia's understanding of an important issue in the state. This is just one of many Agency efforts that demonstrates EPA's commitment to cooperative federalism.

If you have any questions or concerns, do not hesitate to contact me at (919) 541-2107 or via email at Watkins.tim@epa.gov or Brian Schumacher at (702) 798-2242 or via email at Schumacher.brian@epa.gov. I look forward to our continued work together.

Sincerely,

Timothy H Watkins

Timothy H. Watkins
Director

Enclosure

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PFAS Associated with Air Emission Control Devices in West Virginia

Laboratory Data Report #1: Targeted Analysis of PFAS in EPA Method 0010 Sampling Trains

Background. The West Virginia Department of Air Quality (WV DAQ), in coordination with EPA Region 3, requested the Office of Research and Development's (ORD's) technical support in analyzing per- and polyfluoroalkyl substances (PFAS) that may be generated from the Chemours Washington Works facility near Parkersburg, West Virginia, and emitted into surrounding environmental media through air emissions.

Contractors for Chemours conducted stack emissions testing at several locations within the fluoropolymers manufacturing area of the facility in August and November 2018 using standard EPA Method 0010 (also referred to as Modified Method 5 or MM5) sampling trains to identify the specific PFAS compounds and their degradation products that may be emitted to the atmosphere. TestAmerica laboratories extracted samples from the MM5 samples using methanol and analyzed them in their laboratories. At WV DAQ's request, TestAmerica also prepared splits of the extracted samples from three of the emission control points and provided them to ORD[1]. WV DAQ is particularly interested in having ORD quantify the specific PFAS compounds, C3 dimer acid (HFPO-DA) (also known as "GenX"), perfluorinated octanoic acid (PFOA) (also known as C8), and heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether, hereafter referred to as fluoroether (E-1), as well as to identify other PFAS that may occur within the samples. The ORD laboratory does not currently have the instrument capability to analyze E-1, as discussed with WV DAQ, and analytical results for this compound are not presented in this report.

This 1st report includes targeted analysis results for the methanol extracted samples that include 84 stack samples and 32 field quality control (QC) samples. Sample extracts were received at ORD's laboratories in Research Triangle Park, N.C. on April 3, 2019 and analyzed under the direction of Dr. James McCord following targeted analysis procedures. ORD's analysis and report team that contributed to this effort are listed in Table 1.

Table 1. EPA Office of Research and Development Lab Analysis and Report Team.

Responsibility	Personnel
ORD Principal Investigators	James McCord, Mark Strynar, Jeff Ryan
Laboratory chemistry	James McCord
Quality Assurance Review	Sania Tong-Argao
Management coordination and review	Myriam Medina-Vera, Brian Schumacher, Kate Sullivan
Report preparation	Kate Sullivan

[1] U.S. EPA National Exposure Research Laboratory, Project Study Plan: Targeted and Non-targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) In Air Emission Control Devices for the West Virginia Department of Air Quality (WVDAQ) D-IO-0031870-QP-1-0, 19Feb2019.

The current data report provides a simple representation and summary of targeted analysis results. Therefore, the description of methods and quality assurance are brief and high-level. Additional reports and/or publications may be developed that will include a more detailed description of methods, quality assurance procedures and interpretation of data[1]. As study partners/collaborators, we anticipate that WV DAQ and Region 3 will assist in these reports and publications.

Methods in Brief. EPA Method 0010 (also referred to as Modified Method 5 or MM5) sample train extracts were analyzed by ultra-performance liquid chromatography mass spectrometry (UPLC-MS) using targeted workflow methods described within our laboratory Quality Assurance Project Plan[2] and McCord *et al.* 2019[3]. Methanol extracts were provided to ORD in vials containing approximately 5 or 50 mL of sample. Samples were subsampled as received, diluted if necessary, and analyzed by UPLC-MS against a calibration curve of authentic standards prepared in laboratory reagent solvents. A Waters Acquity ultra performance liquid chromatograph (UPLC) coupled to a Waters Xevo TQ-S micro triple quadrupole mass spectrometer was used for analysis of HFPO-DA; an Orbitrap Fusion LC-MS operating in pseudo triple quad mode was used for analysis of PFOA.

Characteristics of PFOA and HFPO-DA are provided in Table 2, including formula, monoisotopic mass, CAS registry number (CASRN) and the CompTox DSSTox substance identifier (DTXSID) for each compound. Additional information about these compounds can be obtained from EPA's Comptox Chemistry Dashboard (https://comptox.epa.gov/dashboard) (U.S. EPA CompTox, 2019)[4].

PFOA and HFPO-DA concentrations were determined via calibration curves derived from authentic standards using a traditional targeted UPLC-MS/MS approach. There is a wide range in compound concentrations across the extracted samples that required dilution of some samples. Concentrations were calibrated with external standards. PFOA was calibrated within the range from 0.5 to 250 ng/mL. HFPO-DA was calibrated within the range from 10 to 10,000 ng/mL. ORD received splits of original samples, concentrations are provided as ng/mL of sample in the vial. Correlation of the measured concentrations to levels in air, emissions volumes, etc. was not carried out.

We determined PFAS presence and concentrations based on acceptable chromatographic peaks and spectral data (Table 3). Samples with no identifiable peak are labeled Non-Detect ("ND") and samples with concentrations below the calibration range (i.e. Limit of Quantitation, LOQ) are flagged "U". Samples that initially exceed the upper calibration range are flagged "JC1". Table 3 provides the dilution factors used to process stack samples (flagged D# where # equals

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[2] National Exposure Research Laboratory Quality Assurance Project Plan: Targeted analyses of Per- and Polyfluoroalkyl Substances (PFAS) in Liquid Samples. J-WECD-0031917-QP-1-0. May 2019.

[3] McCord, J., Strynar, M. Identifying Per- and Polyfluorinated Chemical Species with a Combined Targeted and Non-Targeted-Screening High-Resolution Mass Spectrometry Workflow. *J. Vis. Exp.* (146), e59142, doi:10.3791/59142 (2019). https://www.jove.com/video/59142/identifying-per-polyfluorinated-chemical-species-with-combined.

[4] U.S. EPA CompTox Chemistry Dashboard https://comptox.epa.gov/dashboard.

the dilution factor). The calibration range was adjusted by the dilution factor when applying the "U" and "JC1" flags.

Results. Table 3 provides concentrations for the sample extracts. MM5 sampling trains (3 runs) were conducted at the inlet and outlets of emission control devices at 3 locations in the facility for a total of 7 sample trains (see the project study plan[1] appendices for details of sample testing provided by Chemours). Sample identifiers are as provided by TestAmerica on their chain of custody (CoC) forms. Four extracted samples were produced from each MM5 sample train:

- Front-Half Composite—consisting of a particulate filter, and a probe, nozzle and front portion of the filter holder bell housing glassware solvent rinses,
- Back-Half Composite—consisting of an XAD-2 resin module, and the back portion of the filter holder bell housing with connecting glassware solvent rinses,
- Condensate and Impinger Contents—consisting of the D.I. Water content used to initially charge the impingers and Condensate collected during the sampling run, and
- Breakthrough XAD-2 Resin Tube—consisting of a standard XAD-2 module placed behind the Condensate Impingers as a final quality assurance indicator of the lack of breakthrough of the HFPO-DA through the sampling train.

The tabular presentation is organized to facilitate comparison of inlet and outlet compound abundance at each of the sampling locations. Table 3 provides results for the PTFE inlet and outlet samples collected on August 24, 2018; the PFA scrubber inlet and outlet samples collected on November 6, 2018; and the FEP inlet lines 2 and 3 and scrubber outlet collected on November 7, 2018.

PFOA was not detected or had low concentrations (<200 ng/mL) in many of the samples except for the set of samples from the PFA Scrubber Inlet which had somewhat higher concentrations. HFPO-DA was observed in most samples at markedly higher vial concentrations than PFOA. HFPO-DA vial concentrations were highest in the inlet locations and generally lower at outlet sampling locations.

Field QC Summary. Table 4 provides concentrations of PFAS in the 32 field quality control samples collected during the two field sampling campaigns. Note that HFPO-DA was observed in some of the field QC samples at concentrations greater than the limit of quantitation (>LOQ). However, we did not receive sufficient information about the field quality assurance (QA) samples to associate contaminated blanks with potentially impacted samples; therefore, the data are not qualified. We used a variety of process blanks to account for any PFAS contamination that may have occurred during laboratory analysis. Samples were processed with 24 laboratory blanks that were free of PFOA and HFPO-DA.

Table 2. Priority Analytes of Interest for WV DAQ for Targeted Analysis.

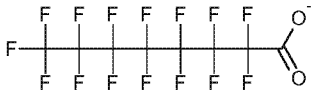
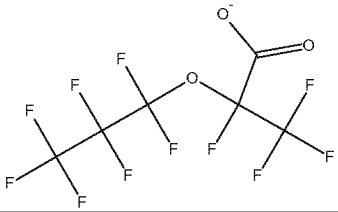
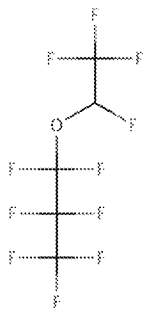
Short Name	Chemical Name	Formula	Monoisotopic Mass (Da)	CAS Registry Number	DTSXID and Compound Structure
PFOA	Perfluorooctanoic Acid	$C_8HF_{15}O_2$	413.9737	335-67-1	DTXSID8031865 
HFPO-DA (GenX)	Hexafluoropropylene oxide dimer acid	$C_6HF_{11}O_3$	329.9750	13252-13-6	DTXSID70880215 
E-1	Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether	$C_5HF_{11}O$	285.9852	3330-15-2	DTXSID8052017 

Table 3. PFAS Concentrations in MM5 Sample Extracts Determined with Targeted Analysis.

Location	MM-0010 Fraction	Run	Sample ID	PFOA ng/mL in vial		HFPO-DA ng/mL in vial	
PTFE Inlet	FH filter fraction composite	Run 1	12505-1	0.1	U	792	
		Run2	12505-5	0.4	U	1,450	
		Run3	12505-9	0.3	U	1,420	
	BH filter fraction composite	Run 1	12505-2	1.0		23,400	D10
		Run2	12505-6	1.5		15,300	D10
		Run3	12505-10	3.7		60,100	D100
	Impinger condensate	Run 1	12505-3	1.4		23,100	D10
		Run2	12505-7	1.4		15,300	D10
		Run3	12505-11	1.6		19,100	D10
	XAD-2 resin tube	Run 1	12505-4	0.2	U	8,590	D10
		Run2	12505-8	0.2	U	4,540	D10
		Run3	12505-12	0.6		8,600	D10
PTFE Outlet	FH filter fraction composite	Run 1	12503-1	0.6		555	
		Run2	12503-5	1.2		1,040	
		Run3	12503-9	0.9		879	
	BH filter fraction composite	Run 1	12503-2	0.4	U	91.2	
		Run2	12503-6	0.1	U	91.4	
		Run3	12503-10	0.3	U	75	
	Impinger condensate	Run 1	12503-3	ND		ND	
		Run2	12503-7	ND		ND	
		Run3	12503-11	ND		ND	
	XAD-2 resin tube	Run 1	12503-4	ND		64.2	
		Run2	12503-8	ND		ND	
		Run3	12503-12	ND		ND	
PFA Scrubber Inlet	FH filter fraction composite	Run 1	13273-1	0.3	U	95.3	
		Run2	13273-5	0.8		280	
		Run3	13273-9	0.5		186	
	BH filter fraction composite	Run 1	13273-2	68		16,200	D10
		Run2	13273-6	313	JC1	33,800	D50
		Run3	13273-10	76.8		12,500	D10
	Impinger condensate	Run 1	13273-3	295	JC1	132,000	D200
		Run2	13273-7	317	JC1	207,000	D200
		Run3	13273-11	354	JC1	142,000	D100
	XAD-2 resin tube	Run 1	13273-4	0.5	U	796	
		Run2	13273-8	0.5	U	1,450	
		Run3	13273-12	0.4	U	516	
PFA Scrubber Outlet	FH filter fraction composite	Run 1	13274-1	ND		530	
		Run2	13274-5	4.7		699	
		Run3	13274-9	4.2		482	
	BH filter fraction composite	Run 1	13274-2	4.0		3,610	D10
		Run2	13274-6	2.7		3,330	D10
		Run3	13274-10	2.8		7,560	
	Impinger condensate	Run 1	13274-3	ND		35.6	
		Run2	13274-7	ND		ND	
		Run3	13274-11	ND		20.8	
	XAD-2 resin tube	Run 1	13274-4	ND		ND	
		Run2	13274-8	ND		ND	
		Run3	13274-12	ND		ND	

ND	Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.
U	LOQ: Peak area detected but concentration less than the concentration of the lowest standard calibration curve.
D#	Sample is diluted by the factor indicated.
JC1	Sample result exceeds the upper calibration range.

Table 3. PFAS Concentrations in MM5 Samples Determined with Targeted Analysis (continued).

Location	MM-0010 Fraction	Run	Sample ID	PFOA ng/mL in vial		HFPO-DA ng/mL in vial	
FEP Line 2 Inlet	FH filter fraction composite	Run 1	13312-1	3.6		6,310	
		Run2	13312-5	3.0		3,840	
		Run3	13312-9	3.7		2,210	
	BH filter fraction composite	Run 1	13312-2	16.2		8,210	
		Run2	13312-6	4.2		4,170	
		Run3	13312-10	7.5		8,420	
	Impinger condensate	Run 1	13312-3	111		89,900	D100
		Run2	13312-7	111		62,800	D100
		Run3	13312-11	110		87,800	D100
	XAD-2 Resin Tube	Run 1	13312-4	ND		ND	
		Run2	13312-8	0.03	U	132	
		Run3	13312-12	ND		181	
FEP Line 3 Inlet	FH filter fraction composite	Run 1	13315-1	13.9		9,860	D10
		Run2	13315-5	6.4		2,140	
		Run3	13315-9	11.9		5,730	D10
	BH filter fraction composite	Run 1	13315-2	21.8		8,170	
		Run2	13315-6	30.4		3,390	
		Run3	13315-10	30.1		3,820	D10
	Impinger condensate	Run 1	13315-3	142		122,000	D100
		Run2	13315-7	117		90,900	D20
		Run3	13315-11	127		106,000	D100
	XAD-2 resin tube	Run 1	13315-4	0.4	U	89.2	
		Run2	13315-8	0.02	U	33.7	
		Run3	13315-12	0.04	U	19.2	
FEP Scrubber Outlet	FH filter fraction composite	Run 1	13316-1	1.7		64.8	
		Run2	13316-5	2.2		35.7	
		Run3	13316-9	2.4		43.7	
	BH filter fraction composite	Run 1	13316-2	0.6		159	
		Run2	13316-6	0.4	U	21.1	
		Run3	13316-10	0.1	U	30.4	
	Impinger condensate	Run 1	13316-3	ND		ND	
		Run2	13316-7	ND		ND	
		Run3	13316-11	ND		ND	
	XAD-2 resin tube	Run 1	13316-4	ND		32.7	
		Run2	13316-8	ND		ND	
		Run3	13316-12	ND		18.4	

ND	Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.
U	LOQ: Peak area detected but concentration less than the concentration of the lowest standard calibration curve.
D#	Sample is diluted by the factor indicated.
JC1	Sample result exceeds the upper calibration range.

Table 4. PFAS Concentrations in QC Samples Collected in the Field.

			PFOA		HFPO-DA	
Location	MM-0010 Fraction	Sample ID	ng/mL in vial		ng/mL in vial	
Field QC: Blank Train Samples 8/20/2018	QC M0010 FH BT	12459-13	ND		ND	
	QC M0010 BH BT	12459-14	ND		67.6	
	QC M0010 Impingers 1,2&3 Condensate TB	12459-15	ND		ND	
	QC M0010 Breakthrough XAD-2 Resin Tube	12459-16	ND		ND	
	QC N0010 DI Water RB	12459-17	ND		ND	
	QC M0010 MEOH with 5% NH4OH RB	12459-18	ND		ND	
	QC M0010 XAD-2 Resin Tube RB	12459-19	ND		98.7	
	QC M0010 MEOH with 5% NH4OH TB	12459-20	ND		ND	
	QC M0010 XAD-2 Resin Tube TB	12459-21	ND		ND	
	QC M0010 Combined glassware rinses PB	12459-22	ND		ND	
Field QC: Blank Train Samples 11/8/2018	FEP QC M0010 FH BT	13314-1	0.3	U	17.0	
	FEP QC M0010 BH BT	13314-2	0.1	U	30.2	
	FEP QC M0010 Impingers 1,2&3 Condensate BT	13314-3	ND		2.7	U
	FEP QC M0010 Breakthrough XAD-2 BT	13314-4	ND		ND	
	FEP QC M0010 Combined glassware rinses PB	13314-5	ND		ND	
	FEP QC M0010 MEOH with 5% HN4OH RB	13314-6	ND		ND	
	FEP QC M0010 XAD-2 Resin Tube RB	13314-7	ND		ND	
	FEP QC M0010 DI Water RB	13314-8	ND		ND	
	FEP QC M0010 XAD-2 Resin Tube TB	13314-9	ND		ND	
Field QC: MB Samples	QC Field MB	427249	ND		ND	
	QC Field MB	427579	ND		ND	
	QC Field MB	427721	ND		39.5	
	QC Field MB	428539	ND		ND	
	QC Field MB	428541	ND		ND	
	QC Field MB	428730	ND		ND	
	QC Field MB	436766	ND		ND	
	QC Field MB	437214	no data		ND	
	QC Field MB	437217	no data		40.6	
	QC Field MB	437337	ND		ND	
	QC Field MB	437700	ND		32.6	
	QC Field MB	438058	ND		ND	
	QC Field MB	438059	ND		ND	

ND Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.

U LOQ: Peak area detected but concentration less than the concentration of the lowest standard calibration curve.